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14. ABSTRACT

We have synthesized a liquid-crystalline monomer, 12-[4-cyanobiphenyl-4'-oxy] dodecanoic acid (11CN-COOH), and then grafted it onto the DABPA and then cured the 11CN-COOH-grafted DABPA with BMPM, yielding BMI resin functionalized with liquid crystal monomer. In so doing, we have elucidated the reaction (cure) mechanism between 11CN-COOH-grafted DABPA and BMPM using Fourier transform infrared (FTIR) spectroscopy. Thermal transition temperatures before and after the cure of BMI resin and also functionalized BMI resin were measured using differential scanning calorimetry. Micrographs of BMI resin and also functionalized BMI resin were obtained using optical microscopy. Finally, the mechanical properties of cured BMI and functionalized BMI resins were measured. It has been found that the flexural modulus of functionalized BMI resin is about two times greater than that of neat BMI resin, indicating that the addition of liquid crystalline monomer has enhanced the toughness of BMI resin.

15. SUBJECT TERMS

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Project Title: NANOSTRUCTURED HIGH-PERFORMANCE MATERIALS
CONSISTING OF BISMALEIMIDE AND FUNCTIONAL LIQUID
CRYSTAL MONOMER

AFOSR Grant Number: F49620-02-1-0023

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PROJECT SUMMARY

Bismaleimide (BMI) resinis usually obtained by reacting 4,4'-bismaleimidodiphenyl-methane (BMPM) with diallylbisphenol A (DABPA) and curing the mixture at an elevated temperature. While cured BMI resin has a very high glass transition temperature (T_g) (250-300 °C) compared to the T_g (120 °C) of cured epoxy resin, BMI resin is very brittle. In order to overcome such weaknesses of BMI resin, in the present project we have synthesized a liquid-crystalline monomer, 12-[4-cyanobiphenyl-4'-oxy] dodecanoic acid (11CN-COOH), and then grafted it onto the DABPA and then cured the 11CN-COOH-grafted DABPA with BMPM, yielding BMI resin functionalized with liquid crystal monomer. In so doing, we have elucidated the reaction (cure) mechanism between 11CN-COOH-grafted DABPA and BMPM using Fourier transform infrared (FTIR) spectroscopy. For comparison, we also investigated cure mechanism of neat BMI resin (without a liquid crystal monomer). Thermal transition temperatures before and after the cure of BMI resin and also functionalized BMI resin were measured using differential scanning calorimetry. Micrographs of BMI resin and also functionalized BMI resin were obtained using optical microscopy. Finally, the mechanical properties of cured BMI and functionalized BMI resins were measured. It has been found that the flexural modulus of functionalized BMI resin is about two times greater than that of neat BMI resin, indicating that the addition of liquid crystalline monomer has enhanced the toughness of BMI resin.

Table of Content

1. Background

During the past two decades, numerous research groups have investigated the mechanical and thermal properties of epoxy resin and its composites with glass or carbon fibers. There are too many papers to cite them all here. Thus some selected papers are cited here [1 – 9]. Although epoxy composite materials have successfully been used for certain structural applications (e.g., airplanes), they suffer from two weaknesses. One weakness lies in that they cannot be used for high-temperature structural applications, owing to low glass transition temperature (T_g) (approximately 120 °C) of cured epoxy resin. Another weakness is a relatively high moisture absorptivity. In addition, the density of carbon fiber, for example, is much higher than the density of epoxy resin, and thus the high weight-to-volume ratio for carbon fiber-epoxy composite poses problems for certain structural applications. For that reason, some efforts were spent on investigating aramid fiber-epoxy composites [10]. However, a real technical problem unresolved yet lies in the insufficient adhesion between the carbon or aramid fibers and the epoxy resin matrix although sizing chemicals were used. To overcome such an inherent problem, the concept of molecular composites [11, 12] has been suggested.

In the recent past, some research groups have synthesized liquid-crystalline epoxy resin systems [13 – 15] and others [16, 17] investigated their mechanical properties. In those investigations, liquid-crystalline segments were part of an epoxy resin, so that the liquid-crystalline segments could form a separate phase during the cure of an epoxy resin. However, cured liquid-crystalline epoxy suffers from relatively low thermal stability associated with the low T_g of epoxy resin.

In order to overcome the deficiency of epoxy resin in high-temperature applications, efforts have been made to replace epoxy resin with bismaleimide (BMI) resin, which has a very high T_g (250-300 °C) compared to the T_g (120 °C) of cured epoxy resin. As a matter of fact, BMI resin is available commercially (Ciba-Geigy Group). However, BMI resin is *not* without weakness in certain properties, namely it is very brittle and has a high moisture absorptivity. In order to overcome such weaknesses of BMI resin, more than about a decade ago an attempt was made to synthesize liquid-crystalline BMI in a research laboratory [18, 19]. In those studies, the monomers were end-capped with maleimide, nadimide, or methylnadimide functinalities. However, the curing reaction proceeded in an uncontrollable manner and the cured network was found to be brittle because of high crosslinking density. Further such an attempt, though elegant conceptually, has received *little* attention from both the academic and industrial communities. At present there are no liquid-crystalline BMI available commercially.

During the period of this project we have synthesized a liquid-crystalline (LC) monomer, 12-[4-cyanobiphenyl-4'-oxy] dodecanoic acid, and then grafted it onto the backbone of a commercial BMI resin. In so doing, we have characterized the cure neat BMI resin and cured liquid-crystalline BMI, and investigated their phase morphology, and the mechanical properties.

2. Experimental Section

2.1 Materials

4,4′– Bismaleimidodiphenylmethane (BMPM, Matrimid® 5292 A) and diallylbisphenol A (DABPA, Matrimid® 5292 B) were provided by Ciba-Geigy Corp. BMPM was recrystallized from mixed solvent of methanol and chloroform (1:1 vol/vol) before use. It was confirmed via differential scanning calorimetry (DSC, TA modulated 2920) that BMPM had no melting point. DABPA was used as received. 4-cyano- 4′ -hydroxy biphenyl (HBPN) having purity 95 % (TCI America) was used as received. 12-bromododecanoic acid having purity 95 % (Aldrich) was used as received. N-N-Dimethyl formamide (DMF) and acetone were refluxed in the presence of calcium hydride powder (CaH$_2$, Aldrich) and then distilled under reduced pressure. After distillation, dry DMF was kept with anhydrous calcium chloride (CaCl$_2$, 4-20 mesh) (Fisher Scientific) to remove water.

2.2 Synthesis of Liquid-Crystalline Monomer

We synthesized a liquid-crystalline monomer 12-[4-cyanobiphenyl-4′-oxy] dodecanoic acid, which will be referred to as 11CN-COOH. The reaction route for the synthesis of 11CN-COOH is shown schematically below.
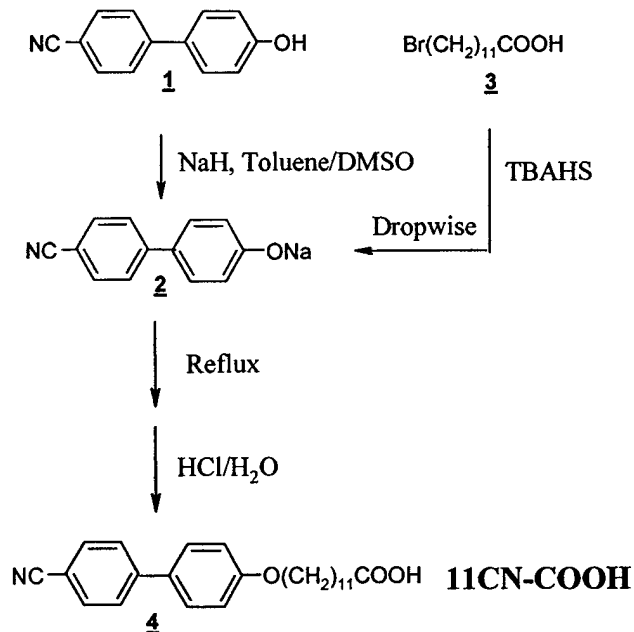

Briefly stated, 11CN-COOH was synthesized as follows. 1 mole of 4-cyano-4′-hydroxyl biphenyl and 1.1 mole of sodium hydride were dissolved into a three-neck flask with 12 ML of mixed solvent consisting of toluene and dimethyl sulfoxide (DMSO) (5:1 v/v). The mixture was stirred for 4 h at room temperature and then the temperature was increased to 60 °C and kept there for 1 h before use. Tetrabutylammonium hydrogen sulfate (TBAHS) was

added to the 12-bromohexanoic acid solution, while stirring for 30 min at 60 °C, which then was added dropwise into a three-neck flask containing 4-cyano-4'-hydroxy biphenyl solution. The mixture was then heated to 80 °C, at which the reaction continued for 24 h. The solution was cooled down to room temperature and then poured into a mixture consisting of 3 M hydrochloric acid (HCl) and water, whereby the reaction product was strongly acidified with HCl solution. After the crude product was precipitated, it was filtered and washed three times with water. The solid obtained was washed three times with a mixed solvent consisting of ethanol and water (1:4 v/v) to remove unreacted 4-cyano-4'-hydroxy biphenyl, filtered, and then dried in a vacuum oven at 50 °C for one day. Finally, the crude product was recrystallized from methanol and then dried in a vacuum oven at 50 °C for two days. ^1H NMR spectra of 11CN-COOH in DMSO and Fourier transform infrared resonance (FTIR) spectroscopy confirmed the completion of reaction.

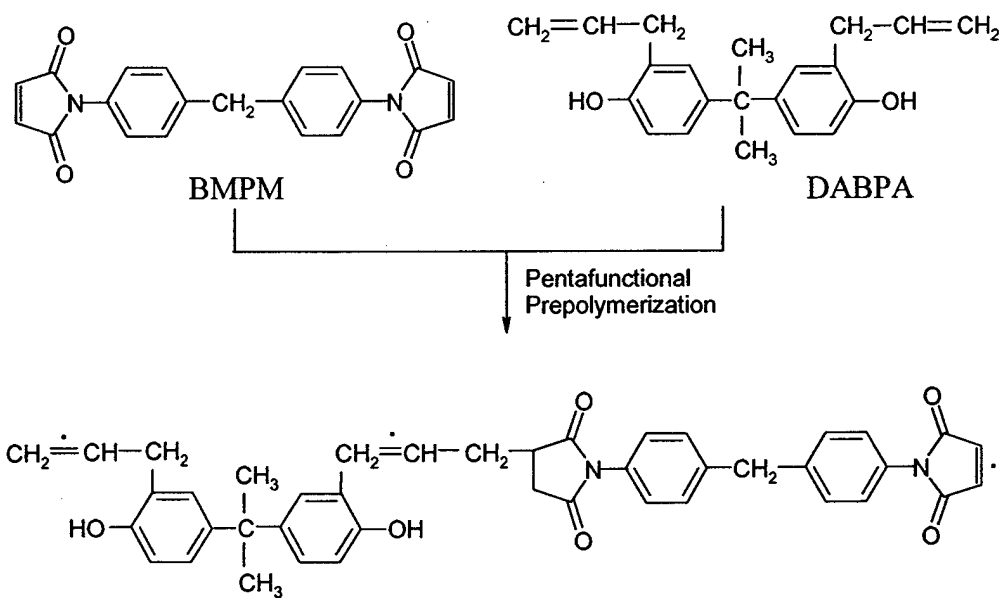### 2.3 Synthesis of Liquid-Crystalline Bismaleimide

1.0 mmol of 12-[4-cyanobiphenyl-4'-oxy] dodecanoic acid (11CN-COOH) was placed into a three-neck flask with 10 mL of anhydrous benzene under agitation at room temperature. 20 mmol of thionyl chloride was dropped into the flask and the mixture was stirred for 30 min at room temperature. Then, the reaction mixture was heated to 80 °C and kept there for 2 h while refluxing. Finally, the crude product, 12-[4-cyanobiphenyl-4'-oxy] dodecanoyl chloride (11CN-COCl), was isolated 5 times from benzene by vacuum distillation, which was then dried under vacuum for 8 h at room temperature. Equimolar amounts of 0.1 mmol of mesogenic chain extender (MCA) and 0.1 mmol of BMPM were mixed and heated to 150 °C, while vigorously stirring for 10 min, in an oil bath under an argon gas atmosphere. Reaction routes for liquid-crystalline BMI are given below in Scheme 1.

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BMPM

3

4
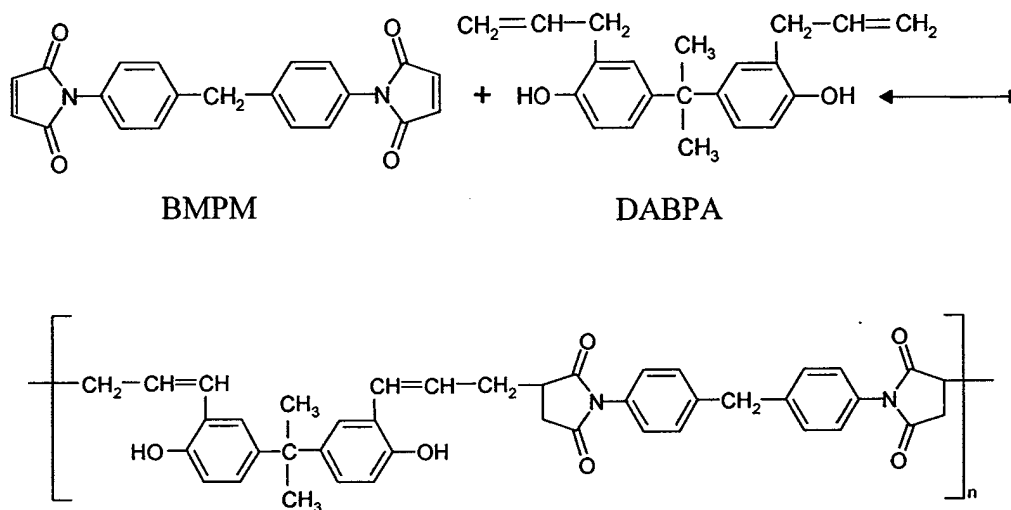
Liquid-crystalline
BMI

5
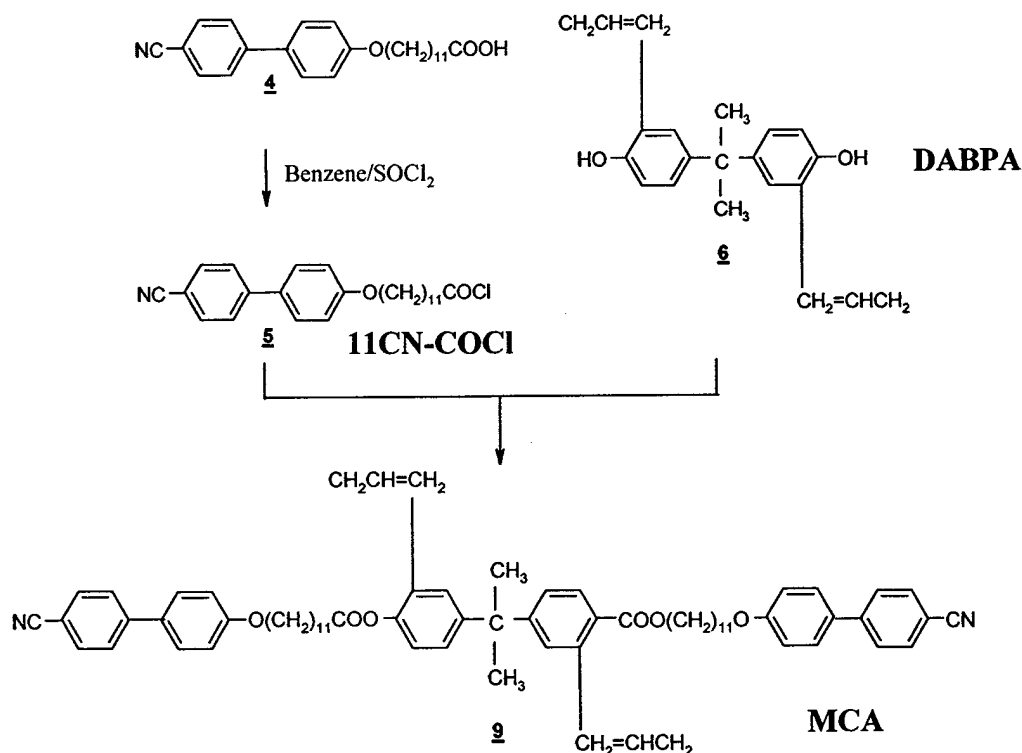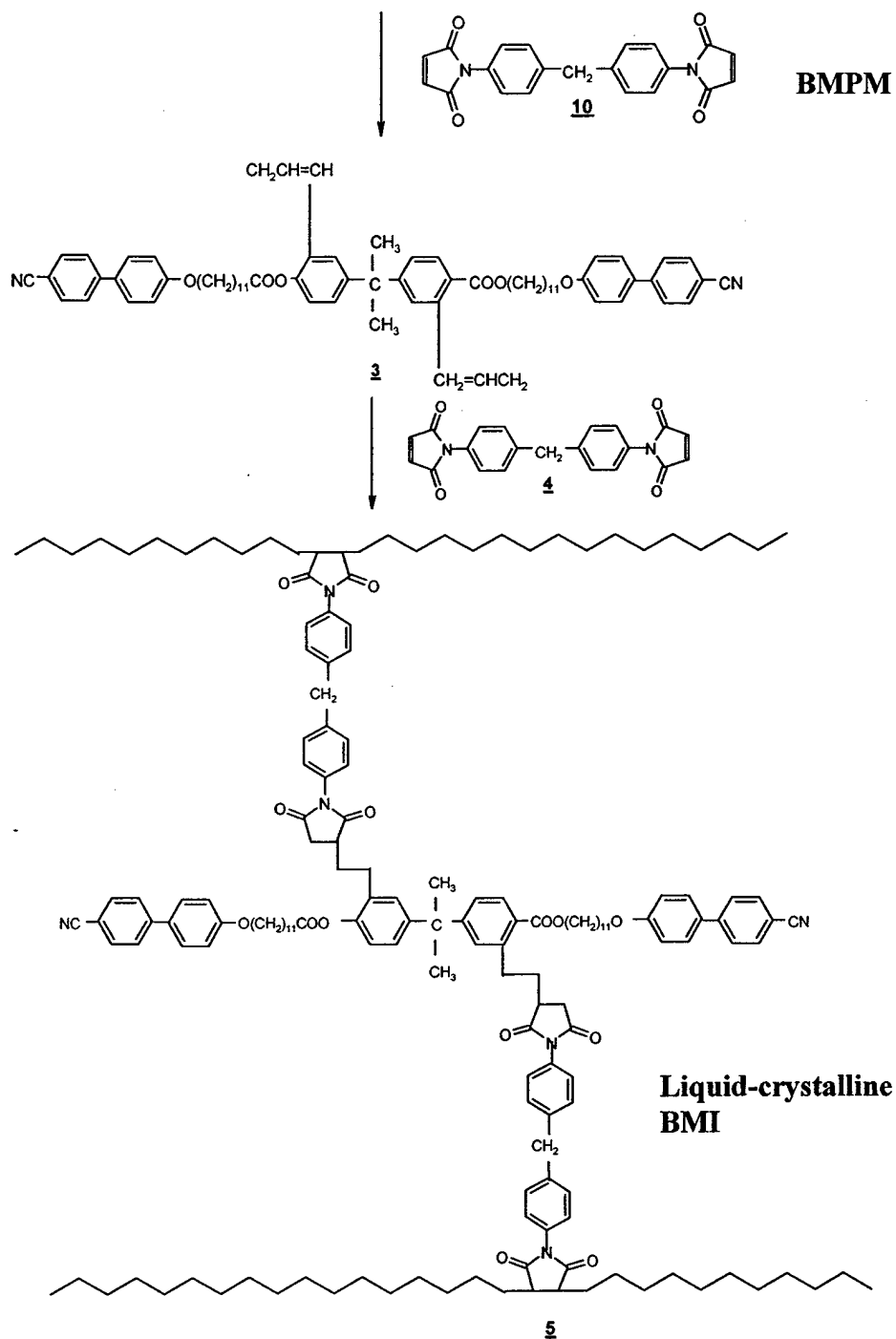
## 2.4 Synthesis of Bismaleimide (BMI)

Equimolar amount (1:1) of each component (BMPM and DABPA) was mixed and heated at 150 °C, while stirring vigorously for 10 min, in an oil bath under an argon atmosphere. The reaction route for the synthesis of BMI is shown below in scheme 2, in which four potential chemical reactions are postulated.

(a) Idealized pentafunctional prepolymer

(b) Ene Reaction

BMPM → Homopolymerization

(c) BMPM homopolymerization

DABPA   BMPM
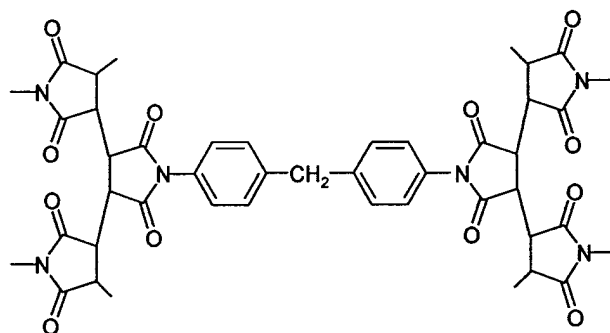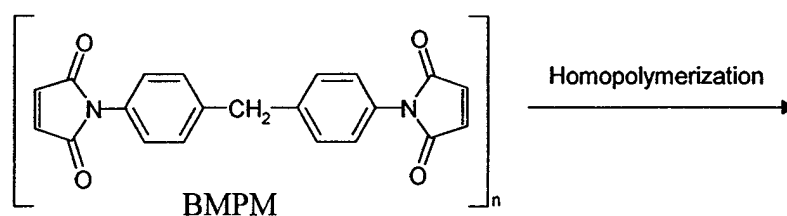
Diels-Alder Reaction

(d) Diels-Alder reaction

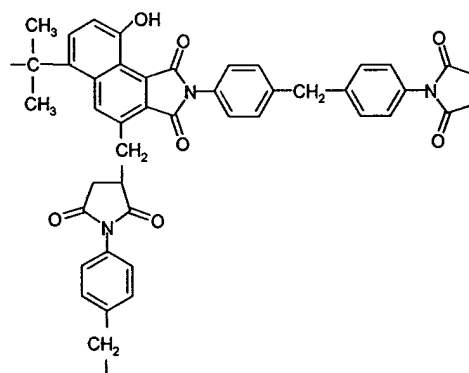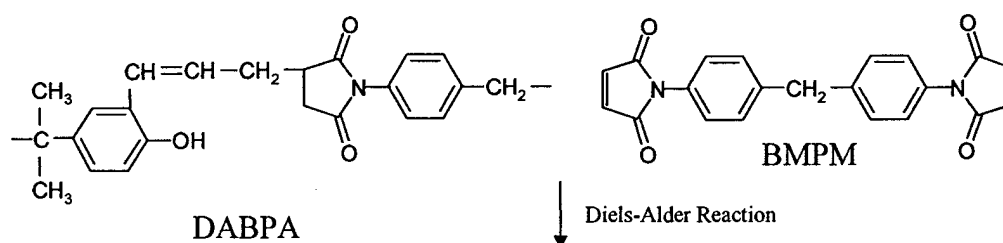**Scheme 2.** Four potential chemical reactions in the BMPM/DABPA system are postulated: (a) idealized pentafunctional prepolymer, (b) Ene reaction, (c) BMPM homopolymerization and (d) Diels-Alder reaction.

2.5 Differential Scanning Calorimety (DSC)

The thermal transition temperatures of liquid crystal monomer 11CN-COOH, BMPM/MCA mixture, and BMPM/DABPA mixture were determined using differential scanning calorimetry (DSC) (Model DSC 2920, TA Instrument) under a nitrogen atmosphere at a heating rate of 20 °C/min. Also, thermo gravimetric analysis (Model TGA 2050, TA Instrument) was conducted to investigate the extent of thermal degradation of the materials at elevated temperatures under a nitrogen atmosphere at a heating rate of 10 °C/min.

2.6 Fourier Transform Infrared (FTIR) Spectroscopy

Using a Fourier ransform infrared spectrometer (16 PC FTIR, Perkin Elmer), FTIR spectra were obtained at room temperature for liquid crystal monomer 11CN-COOH, BMPM/MCA mixtures, and BMPM/DABPA mixtures. Spectral resolution was maintained at 2 cm^{-1}. Dry argon gas was used to purge the sample compartment to reduce the interference of water and carbon dioxide in the spectrum. Thin films were prepared by compression molding to obtain FTIR spectra. Film thickness was adjusted, such that the maximum absorbance of any band was less than 1.0, at which the Beer-Lambert law is valid. Samples were then stored under vacuum until use.

2.7. Transmission Electron Microscopy (TEM)

TEM images of specimens without staining were taken at room temperature using a transmission electron microscope (JEM1200EX 11, JEOL) operated at 120 kV. The ultrathin sectioning (50-70 nm) was performed at room temperature using a Reichert Ultracut E low-temperature sectioning system.

3. Results and Discussion

3.1 Characterization of Cured Liquid-Crystalline BMI Resin

To identify the absorption band in the liquid-crystalline BMI synthesized in this study, we first recorded FTIR spectra of DABPA, 11CN-COOH and MCA at 25 °C in the range of 500–4000 cm^{-1} and they are given in Figure 1. In Figure 1a, the absorption band at 2227 cm^{-1} describes cyano (-CN) group in 11CN-COOH. Figure 1b give the FTIR spectrum for MCA, showing that the absorption band for the hydroxyl group (-OH) at 3350 cm^{-1} in DABPA disappears due to the ester reaction between DABPA and 11CN-COOH. Figure 1c gives the FTIR spectrum for DABPA, showing that the absorption band for the -OH group appears at 3436 cm^{-1} and the absorption band at 3010 cm^{-1} represents the aromatic CH vibration. The absorption band appearing at 1266 cm^{-1} represents the C-O stretching. The characteristic C-O stretching band is shown at 1648 cm^{-1}. Aromatic carbon-carbon double bond (C=C) bands are absorbed at 1612 and 1426 cm^{-1}, respectively. The characteristic absorption band of methylene (CH$_2$) is shown at 1450 cm^{-1}.
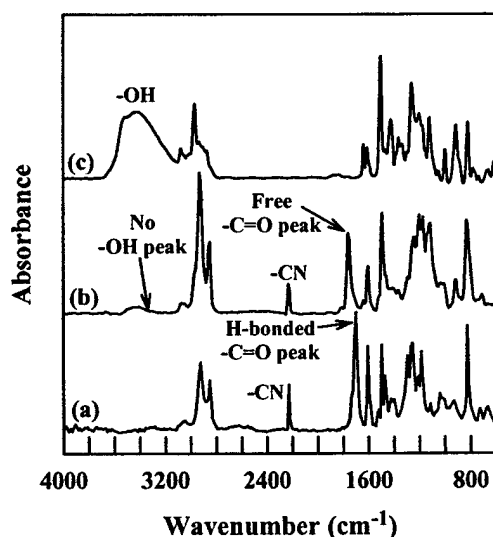
Figure 1. FTIR spectra for (a) 11CN-COOH (b) MCA, and (c) DABPA at 25 °C.

The reactivity of the double bond in the maleimide group is a consequence of the electron withdrawing nature of the two adjacent carbonyl groups, which create an electron deficient double bond. Therefore, BMIs are very susceptible to homopolymerization and copolymerization. Morgan et al. [20] have reported that the reaction scheme for BMPM/ DABPA mixture consists of an addition reaction occurring between the ally groups that are attached to an aromatic ring in DABPA and the double bond of the BMPM. Also, an 'Ene' type linear chain reaction may take place. The resulting substituted styrene undergoes a 'Diels-Alder' reaction with another maleimide group. Once two components have reacted, the BMPM/DABPA 'Ene' adduct prepolymer is considered to be pentafunctional: three double bonds, capable of chain extension and crosslinking and two hydroxyl groups, capable of etherification by hydroxyl dehydration. Potential reactions in the BMPM/DABPA system are shown in Scheme 2.

In-situ FTIR spectroscopy was conducted to monitor the extent of various reactions involved in BMPM/DABPA mixture and BMPM/MCA mixture at different temperatures. With increasing time the following spectral changes have been observed: (i) phenylmale-imide and C-N-C maleimide are converted to phenylsuccinimide and C-N-C succinimide via Ene, Diels-Alder, BMPM homopolymerization, and copolymerization, (ii) vibrational C-H maleimide absorption band decreases rapidly with time, and (iii) allyl double bond of DABPA is decreased by dehydration.

FTIR spectroscopy experiments at steady state were performed to determine the extent of curing reaction between BMPM and DABPA in a mixture during isothermal cure with increasing cure time and at different temperatures. FTIR spectroscopy measurements equipped with a hot plate were performed after films suitable for spectroscopic studies were prepared by directly spreading molten BMPM/DABPA mixture between the KBr disk plates. Temperature was measured at sample surface and controlled to within ± 1 °C using a proportional-integral-derivative (PID) controller. The sample thickness of these films was

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adjusted, such that the maximum absorbance of any band was less than 1.0, at which the Beer-Lambert law is valid. FTIR spectra were obtained using Perkin-Elmer FTIR spectrometer (model 16 PC FTIR). Peak intensity was calculated by integration method using the Gram 386 software. Spectral resolution was maintained at 2 cm^{-1} using 32 scans. Dry argon gas was used to purge the sample compartment to reduce the interference of moisture in the spectrum. Isothermal cure was conducted at 200 °C with various cure periods: 0, 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, 240, 300 and 420 min.

Figure 2a shows how the absorption band associated with the conversion of C-N-C maleimide (centered at 1150 cm^{-1}) to C-N-C succinimide (centered at 1180 cm^{-1}) changes with cure time in the BMPM/DABPA mixture. In addition, the intensity increases, which was induced by the formation of C-N-C succinimide groups. The absorption band of C-N-C maleimide disappears after 100 min. Figure 2b shows a change in the absorption band associated with the conversion of C-N-C maleimide (centered at 1150 cm^{-1}) into C-N-C succinimide (centered at 1180 cm^{-1}) with changing cure time for BMPM/MCA mixture. It can be seen that the intensity rapidly increases in the beginning and then disappears, which was induced by a rapid formation of C-N-C succinimide groups.
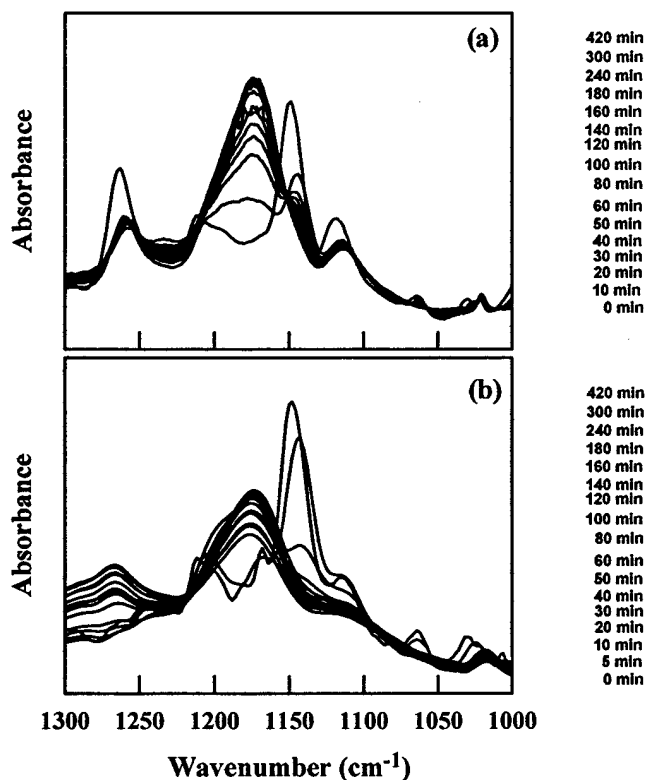

Figure 2. Real-time FTIR spectral changes associated with the conversion of maleimide (1150 cm^{-1}) to succinimide (1180 cm^{-1}) for (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture as a function of time under isothermal cure at 200 °C.

Figure 3a shows how the absorption band associated with the conversion of phenyl-maleimide (centered at 827 cm^{-1}) to phenylsuccinimide (centered at 815 cm^{-1}) changes with cure time in BMPM/DABPA mixture. The absorption band for phenylmaleimide disappears after 100 min. In addition, it can be seen that the absorption band at 975 cm^{-1} corresponding to 2-propenylphenol group increases slowly. In general, the intensity of 2-propenylphenol rapidly decreases with increasing time and temperature. Figure 3b shows how the absorption band associated with the conversion of phenylmaleimide (centered at 827 cm^{-1}) to phenyl-succinimide (centered at 815 cm^{-1}) changes with cure time in BMPM/MCA mixture. The absorption band for phenylmaleimide disappears after 20 min, but the area under the band for phenylsuccinimide is negligibly small for an isothermal cure for 7 h.
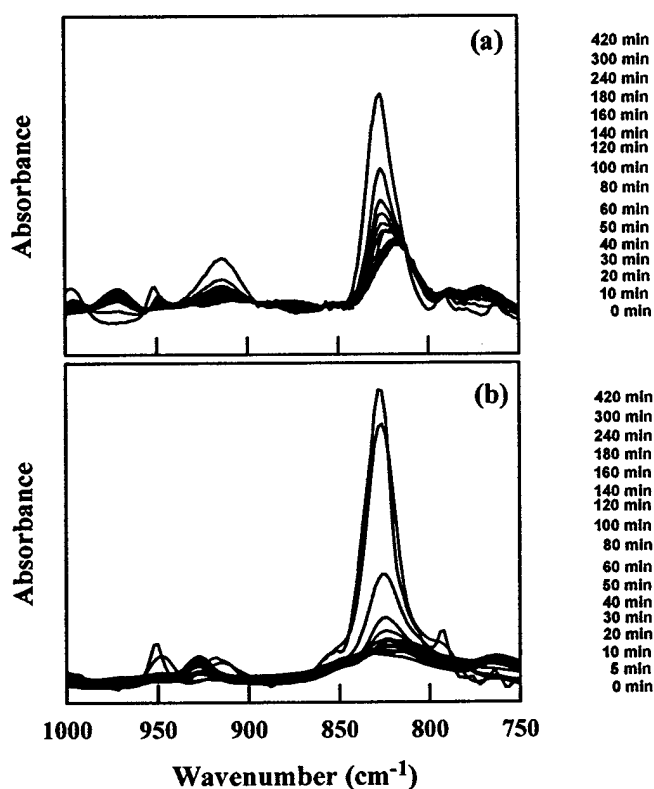

Figure 3. Real-time FTIR spectral changes associated with the conversion of phenyl-maleimide (centered at 827 cm^{-1}) to phenyl succinimide (centered at 815 cm^{-1}) for (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture as a function of time under iso-thermal cure at 200 °C.

In Figure 4, the disappearance of DABPA allyl groups is monitored from the variation in the absorption peak at 914 cm^{-1}. It can be seen that the amount of the allyl group in DABPA (centered at 914 cm^{-1}) decreases rapidly with time up to 180 min and then levels off. The rapid decrease in intensity for the allyl group comes from Ene reaction between the allyl of DABPA and the maleimide of BMPM. The amount of allyl double bond in DABPA does not reach the baseline during the isothermal cure for 7 h.
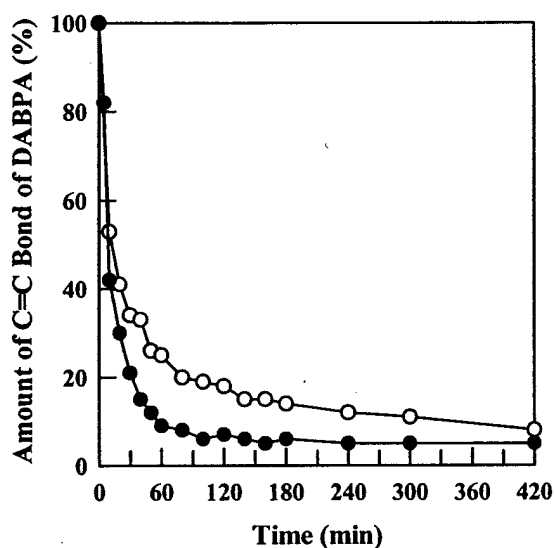
Figure 4. Change of the amount of DABPA allyl groups (914 cm^{-1}) as a function of cure time for BMPM/DABPA (○) (1:1) molar ratio and BMPM/MCA (●) under isothermal cure at 200 °C.

Figure 5 shows the normalized absorbance of CH maleimide at 3100 cm^{-1} for BMPM/DABPA (1:1 molar ratio) and BMPM/MCA mixtures during cure as a function of time at 200 °C. The absence of a CH maleimide absorption band at 3101 cm^{-1} can easily be detected by FTIR spectroscopy. It can be seen that the loss of CH maleimide is stabilized at about 100 min. From the disappearance of CH maleimide corresponding to the formation of succinimide, we can conclude that the conversion of maleimide to succinimide is completed after the BMPM/DABPA mixture was subjected to for ca. 100 min of cure tine at 200 °C.

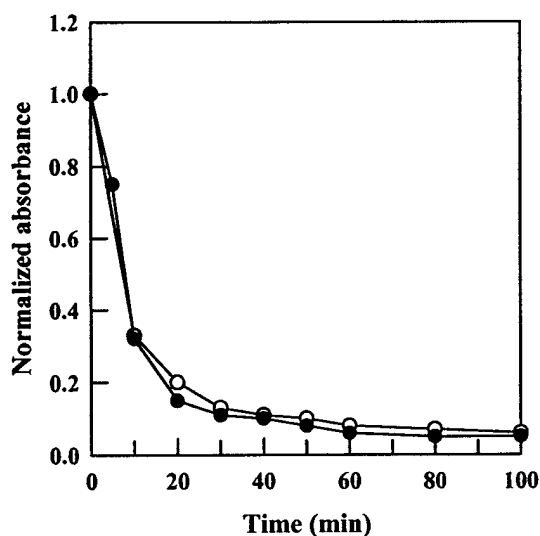**Figure 5.** Change of the amount of CH maleimide (3100 cm^{-1}) as a function of cure time for BMPM/DABPA mixture (○) and BMPM/MCA (●) under isothermal cure at 200 °C.

Figure 6 shows changes of absorption band intensities of hydroxyl group (3473 cm^{-1}) and ether group (C-O-C, 1179 cm^{-1}) as a function of cure time for BMPM/DABPA (1:1 molar ratio) mixture under isothermal cure at 200 °C. It is seen that a simultaneous decrease

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in the hydroxyl band and an increase in the ether band is observed up to 100 min and then they level off. The dehydration of the hydroxyl group of DABPA starts to form ether via homopolymerization even at 200 °C. The mechanism of dehydration is as follows:
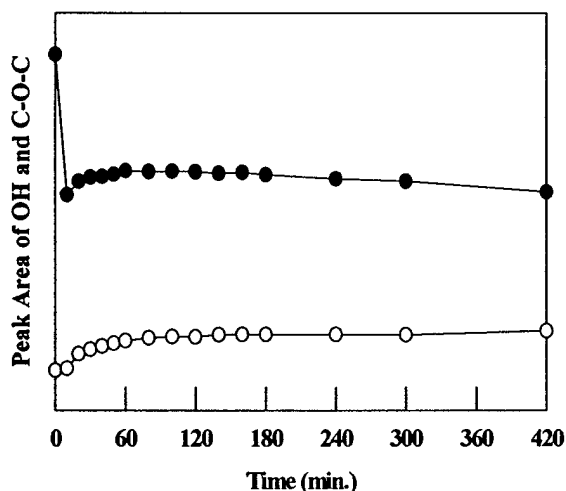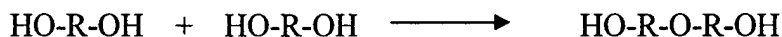
$$\text{HO-R-OH} \quad + \quad \text{HO-R-OH} \quad \longrightarrow \quad \text{HO-R-O-R-OH}$$

Figure 6. Changes of absorption band intensities of hydroxyl (OH, o) and ether (C-O-C, ●) as a function of cure time for BMPM/DABPA mixture under isothermal cure at 200 °C.

The characteristic absorption band assignments for FTIR spectra for BMPM/DABPA resin are summarized in Table 1.

Table 1. Characteristic absorption band assignments of FTIR spectra for BMPM/DABPA mixture and BMPM/MCA mixture

Frequency (cm^{-1})	Main assignments	
	BMPM/DABPA	LCBMI
3100	υ-CH maleimide	υ-CH maleimide
3040	Aromatic CH	Aromatic CH
2920	Aliphatic υ-CH	Aliphatic υ-CH
1710	υ-C=O out of phase	υ-C=O out of phase
1180	υ-C-N-C succinimide	υ-C-N-C succinimide
1150	υ-C-N-C maleimide	υ-C-N-C maleimide
914	DABPA allyl	DABPA allyl
827	Benzene maleimide	Benzene maleimide
815	Benzene succinimide	Benzene succinimide

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Figure 7 describes the degree of cure reaction at 200 °C of BMPM with DABPA without 11CN-COOH (the symbol ○) and with (the symbol ●) 11CN-COOH. It is seen in Figure 7 that the cure reaction (i.e., the conversion of maleimide to succinimide) reached 100 % after about 6 h. The extent of succinimide formation was calculated using eq. 1, in which

$$\left(\frac{(A_{1180}/A_{1710})_t - (A_{1180}/A_{1710})_0}{(A_{1180}/A_{1710})_\infty - (A_{1180}/A_{1710})_0} \right) \qquad (1)$$

the absorption due to the imide carbonyl at 1710 cm^{-1} (A_{1710}) was used as internal reference band. The term $(A_{1180}/A_{1710})_t$ denotes the band absorbance at 1180 cm^{-1} at cure time t, the term $(A_{1180}/A_{1710})_0$ denotes the initial (t = 0) absorbance band at 1180 cm^{-1} before cure began, and the term $(A_{1180}/A_{1710})_\infty$ denotes the absorption band at 1180 cm^{-1} at t = ∞.
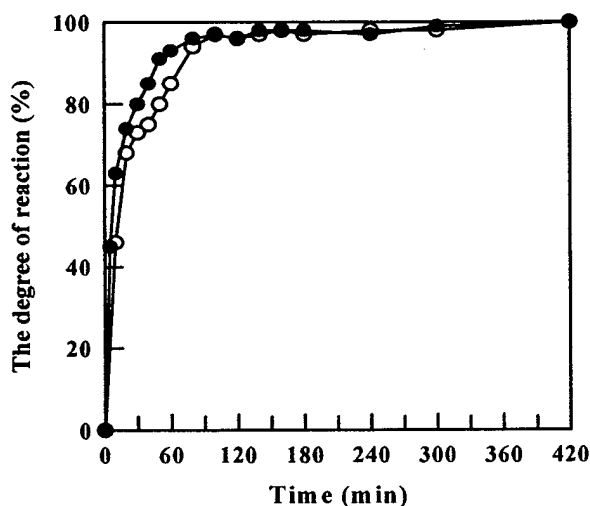

Figure 7. The degree of reaction with respect to cure time of BMPM/DABPA mixture (○) and BMPM/ MCA mixture (●) at 200 °C.
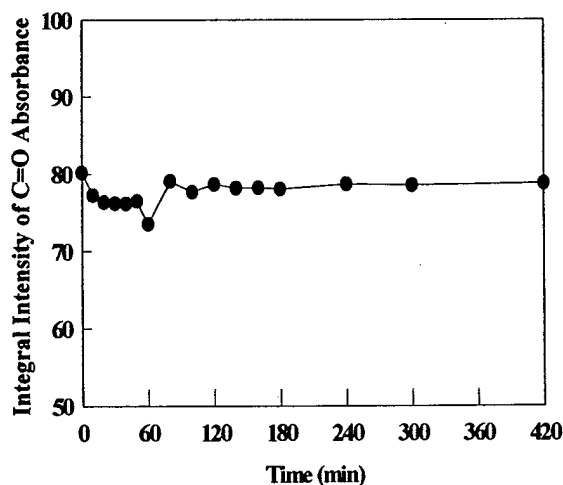

Figure 8. Integral intensity of the of the band in imide carbonyl (C=O) as a function of time for BMPM/DABPA mixture under isothermal cure at 200 °C.

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Figure 8 gives the integral intensity of the absorption band in imide carbonyl (C=O), which is monitored as a function of time. It is seen in Figure 8 that at a given temperature (250 °C) the integral intensity of the absorption band in imide carbonyl (1710 cm^{-1}) is independent of cure time. Therefore, imide carbonyl (C=O) can be used as an internal reference.

3.2 Thermal Transitions in Cured BMI and Cured Liquid-Crystalline BMI

The thermal transitions and thermal stability of BMPM/DABPA and BMPM/MCA mixtures before and after the cure were determined using DSC and TGA, respectively, which were under a nitrogen gas atmosphere at a heating rate of 10 °C /min. The sample size used was about 10 mg, and indium was used to calibrate the temperature and the heat of fusion.

Figure 9 gives DSC traces of (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture before cure begins. It can be seen in Figure 9a that two distinct cure processes take place at 260 and 344 °C. In the temperatures ranging from 200 to 300 °C, a series of chemical reactions occur in the following sequence: (a) the 'Ene' reaction occurs at a significant rate. (b) BMPM homopolymerization reaction occurs. (c) At higher temperatures both 'Ene' homopolymerization and 'Ene-BMPM double bond crosslinking polymerization ('Diels-Alder') reaction occur. (d) Above 240 °C, dehydration of the hydroxyl groups of DABPA starts to occur forming ether crosslinking reaction. In Figure 9b, the BMPM/MCA mixture before cure begins shows multiple thermal transitions, in which the two lower transition peaks are associated with the liquid crystalline phase while the two upper exothermic peaks are associated with curing reaction. The physical origin of the first exothermic peak is not clear although it appears to be associated with the presence of the liquid-crystalline monomer 11CN-COOH attached onto DABPA. The second exothermic peak is related to the cure reaction between BMPM and MCA. Judging from the area under the exothermic peak for the BMPM/MCA mixture, the bulky MCA significantly inhibits cure reaction by steric hindrance. The absence of an extra exothermic peak for the BMPM/MCA mixture, which appeared at
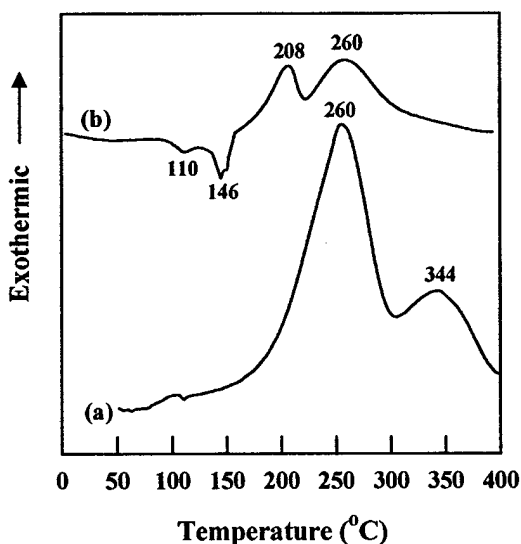

Figure 9. DSC traces of (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture before cure, which were taken at a heating rate of 10 °C /min under a nitrogen atmosphere.

344 °C for the BMPM/DABPA mixture, is due to the increase in mobility provided by the melting of MCA. Therefore, BMPM/MCA mixture does not need high cure temperature.

Figure 10 gives DSC traces of (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture after the cure at 250 °C for 5 h. It is seen in Figure 10a that a high glass transition temperature appears at 253 °C, which is attributable to cure reaction, and an exothermic peak appears at 367 °C. Therefore, the cure at 250 °C for 5 h apparently was not sufficient for completion of cure. The above observations suggest that a post-cure at temperature above 250 °C is needed to complete the cure of BMPM/DABPA mixture. On the contrary, the cured BMPM/MCA mixture does not exhibit evidence of the presence of a liquid crystalline phase over the entire range of temperatures tested (see Figure 10b). We speculate that the absence of liquid crystallinity in the cured BMPM/ MCA mixture is most likely due to the thermal instability of the mesogenic phase in MCA during isothermal cure (i.e., at 250 °C for 6 h).
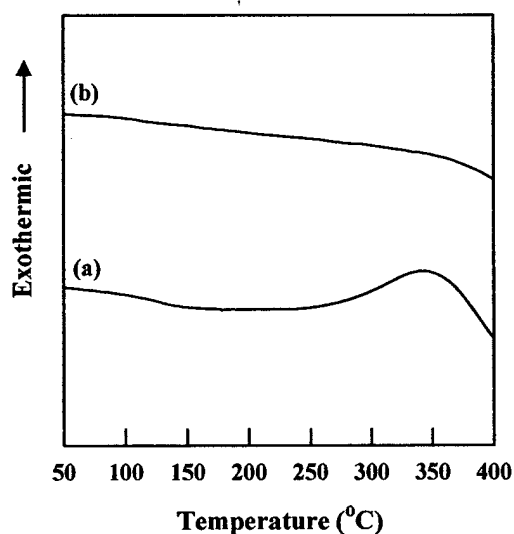

Figure 10. DSC traces of (a) BMPM/DABPA mixture and (b) cured BMPM/MCA mixture, which were taken at a heating rate of 10 °C /min.

Figure 11 gives an optical micrograph of 11CN-COOH and a DSC trace. It is seen in Figure 11 that 11CN-COOH has smectic mesophase and a clearing temperature of 128 °C.
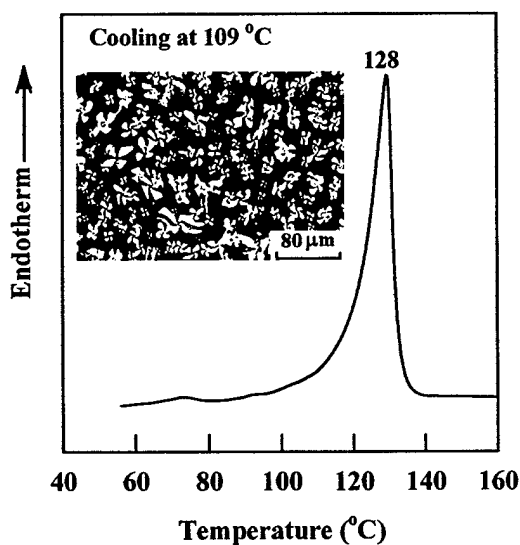

Figure 11. DSC trace of 11CN-COOH in the cooling cycle at a heating rate of 20 °C/min. The morphology 11CN-COOH obtained from polarizing optical microscopy at 109 °C is also given in the inset.

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Figure 12 shows TGA traces for BMPM/DABPA and BMPM/MCA mixtures before cure under a nitrogen gas atmosphere at a heating rate of 10 °C /min. According to the TGA trace in Figure 12a, BMPM/DABPA mixture follows two-step thermal degradation behavior. On the other hand, it is seen from Figure 12b that BMPM/MCA mixture, before cure, is thermally stable at temperatures up to 200 °C while the liquid-crystalline phase in MCA in the BMPM/MCA mixture is thermally less stable than the BMPM/DABPA mixture at temperatures above 350 °C.
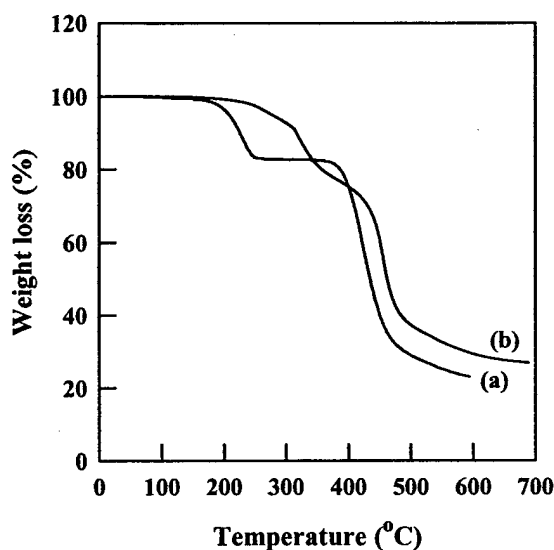
Figure 12. TGA traces of (a) BMPM/DABPA mixture and (b) BMPM/MCA mixture before cure under N_2 atmosphere at a heating rate of 10 °C /min.

Figure 13 gives the TGA traces of BMPM/DABPA and BMPM/MCA mixtures after cure under a nitrogen gas atmosphere at a heating rate of 10 °C /min. The thermal stability of cured BMPM/DABPA and BMPM/MCA mixtures is significantly improved up to 400 °C. It is seen in Figure 13 that only 0.7 % weight loss is recorded at temperatures up to 370 °C.
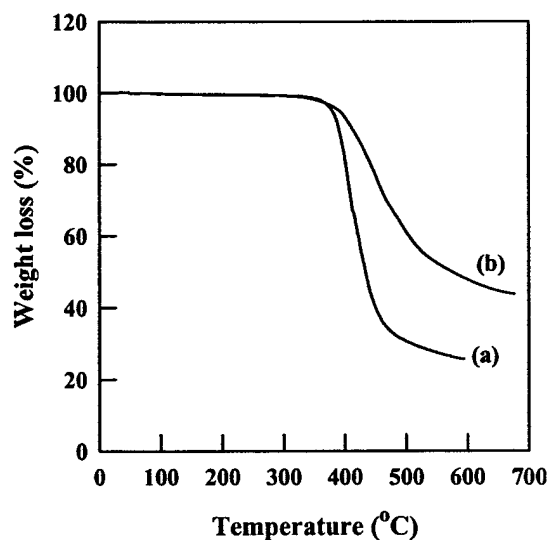
Figure 13. TGA traces of (a) cured BMPM/DABPA mixture and (b) BMPM/MCA mixture under N_2 atmosphere at a heating rate of 10 °C /min.

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3.3 Morphology of Cured Liquid-Crystalline BMI

Figure 14 gives optical micrographs of (a) DABPA attached with 11CN-COOH and (b) BMPM/DABPA mixture in the presence of 11CN-COOH. It is seen in Figure 14 that the size of the liquid-crystalline (11CN-COOH) phase in the BMPM/DBPA mixture (Figure 14b) is much smaller than that attached onto DABPA (Figure 14a).
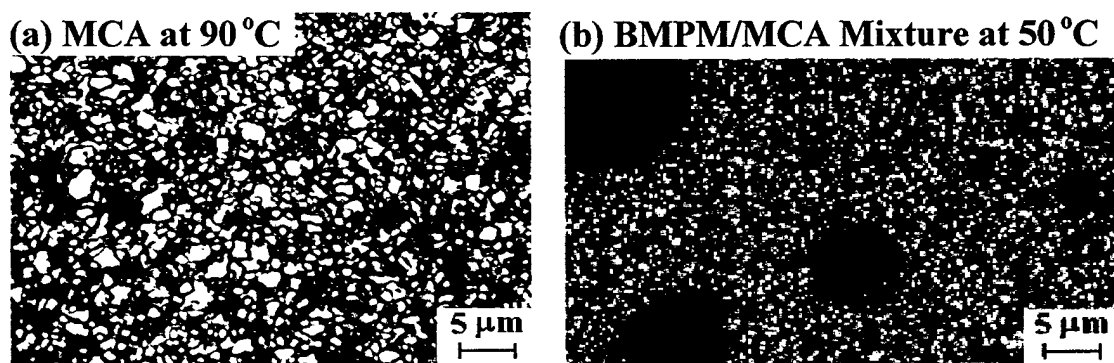

Figure 14. Optical micrographs of (a) DABPA attached with 11CN-COOH (MCA) and (b) BMPM/MCA mixture before cure at 50°C.

Figure 15 gives an optical micrograph of cured BMPM/MCA resin, showing no liquid-crystalline phase. This is attributed to the fact that before reaching the cure temperature for BMI at 250 °C, the mesophase in the liquid crystal monomer 11CN-COOH underwent isotropization.

Figure 15. Optical micrograph of cured BMPM/MCA mixture.

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3.4 Mechanical Properties of Cured Liquid-Crystalline BMI Resin

The mechanical properties of BMI resin have been found to vary significantly with the reactant ratios or cure path (cure time and cure temperature). In the present study, an equimolar ratio of components was mixed and the mixture was heated at 150 °C, while stirring vigorously, in an oil bath for 10 min. Melt was degassed at a reduced pressure for 10 min at 150 °C and then cast onto preheated Teflon mold which was specially designed for flexural, tensile and impact testing specimens. Curing was conducted at 250 °C for 6 h in a convection oven. The flexural properties of the cured BMI resin were measured following ASTM 790, and the impact strength of the cured BMI resin was measured following ASTM 256. Notched specimens were used to measure the impact strength of cured BMPM/DABPA mixture. All specimens were tested at room temperature.

Figure 16 gives the flexural modulus and impact strength of cured BMPM/DABPA resin and cured BMPM/MCA (with liquid-crystalline monomer) mixture. It is seen in Figure 16 that the flexural modulus of cured BMPM/MCA mixture is 4.1 GPa, which is about two times greater than the flexural modulus (2.38 GPa) of cured BMPM/DABPA resin. Although not presented here, we have found that the tensile strength and tensile modulus of cured BMPM/MCA mixture (with liquid-crystalline monomer) are also much higher than the tensile strength and tensile modulus of cured BMPM/DABPA mixture (without liquid-crystalline monomer). Therefore, we can conclude that the addition of liquid-crystalline monomer to BMI resin has enhanced the toughness of BMI.
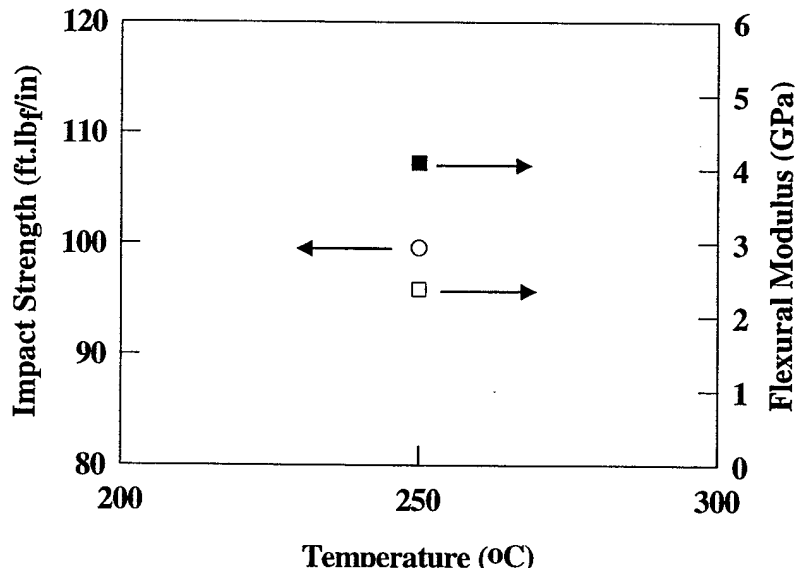

Figure 16. Notched izod impact strength (o) and flexural modulus (□) of cured BMPM/DABPA resin, and flexural modulus (■) of cured BMPM/MCA (with liquid-crystalline monomer) mixture tested at 25 °C.

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